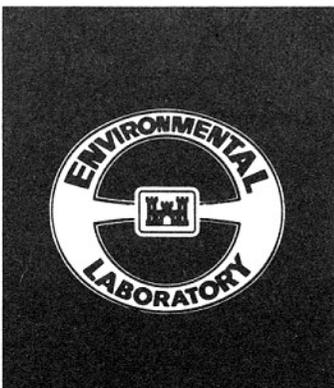
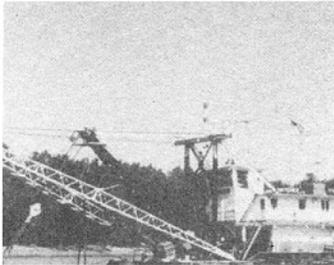




**US Army Corps  
of Engineers**



## **DREDGING OPERATIONS TECHNICAL SUPPORT PROGRAM**

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# **OVERVIEW OF PROCESSES AFFECTING CONTAMINANT RELEASE FROM CONFINED DISPOSAL FACILITIES**

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<b>13. ABSTRACT (Maximum 200 words)</b>  Confined disposal facilities (CDFs) are widely used for the disposal of dredged material from Corps of Engineers maintenance dredging projects along the Atlantic and Gulf coasts and waterways and harbors in the Great Lakes. CDFs are a less common disposal alternative along the Pacific coast and inland river systems. When contaminated dredged material is placed in a CDF, there is a potential for contaminant mobilization and release from the CDF by a variety of physical, chemical, and biological processes.  This report provides an overview of the processes affecting mobilization and release of contaminants from CDFs and the potential applicability of multimedia models for prediction of contaminant release. Processes affecting release from in-water CDFs are emphasized, although many of the processes discussed are applicable to nearshore and upland CDFs. Processes affecting contaminant release are complex, involving a variety of chemicals and operational and design  <span style="float: right;">(Continued)</span>			
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considerations. Many of the important processes are reasonably well known. Laboratory column settling and elutriate techniques have been developed to estimate solids and contaminant concentration in water directly released during hydraulic disposal operations. Predictive techniques for other processes are not as available.

Processes affecting contaminant transport and fate have received considerable attention and have been incorporated into a number of models, primarily for surface waters. Relatively few attempts have been made to consolidate these process descriptions into a unified mechanistic modeling approach applicable to CDFs. Although the limited modeling studies on CDFs have proved valuable in estimating losses in some cases, these approaches are largely unvalidated. No database of sufficient detail to evaluate their general applicability to CDFs presently exists. Some combination of mechanistic modeling and laboratory techniques presently available may be sufficient to provide reconnaissance-level evaluations of CDF containment effectiveness. However, additional model and laboratory test development as well as supporting field studies are needed to develop fully predictive tools. Such tools would provide cost-effective methods for evaluating CDF design and operational alternatives.

## PREFACE

This study was conducted under an Interagency Agreement between the US Army Engineer Waterways Experiment Station (WES) and the Environmental Research Laboratory, US Environmental Protection Agency, Athens, GA (ERL-Athens).

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OVERVIEW OF PROCESSES AFFECTING CONTAMINANT RELEASE  
FROM CONFINED DISPOSAL FACILITIES

PART I: INTRODUCTION

Background

1. Contaminated dredged material is sometimes disposed in confined disposal facilities (CDFs) designed and operated to retain solids and control environmental impacts. Annually, on a national scale, approximately 30 percent of the 290 to 370 million cubic meters of material removed from Federal navigation channels to maintain authorized depths is placed in CDFs (Palermo 1986). This volume of dredged material derives mainly from maintenance dredging for the Atlantic and Gulf Coast harbors and waterways and numerous harbors on the Great Lakes (Palermo 1986).

2. When contaminated dredged material is placed in a CDF, contaminants may be mobilized and transported away from the CDF by a variety of physical, chemical, and biological processes. Although CDFs were designed to retain dredged material solids, contaminants in carrier water (if any) released from the containment area and releases along other contaminant migration pathways may result in mass transfers of contaminants and exposure concentrations that are of environmental significance. For some migration pathways, standard procedures are available for estimation of contaminant mass loss and resulting exposure concentrations. For most, however, standard procedures have not been adopted. Research and development of procedures for preproject estimation of contaminant migration has advanced primarily along the lines of laboratory tests that simulate processes governing mass flux for a pathway. Another approach to preproject estimation of contaminant losses that has been applied to similar disposal problems is transport and fate computer modeling. Therefore, information on the availability and applicability of water quality, groundwater, and other models to CDFs is needed.

Organization and Scope of the Report

3. This report provides an overview of the processes influencing the exposure concentrations and release of contaminants from CDFs. The report

surveys available modeling approaches that may be used to estimate that exposure and release. This report deals primarily with CDFs placed in open water, although many of the processes and modeling techniques discussed are applicable to nearshore (located in lakes, estuaries, and large rivers) and upland CDFs. The remainder of this report is divided into three major parts. First, the processes affecting exposure and release are discussed (Part II). Second, in Part III the available modeling approaches that may have applicability to estimating those exposures and releases are surveyed. Finally, Part IV summarizes the study results and provides recommendations for further research and development.

## PART II: PROCESSES AFFECTING EXPOSURE AND RELEASE

4. Major processes impacting releases and exposure concentrations from CDFs include the physical, chemical, and biological mechanisms that impact the transport and transformations of contaminants. Topics addressed in the succeeding sections are as follows: (a) the first describes some of the general characteristics of CDFs that may impact contaminant releases, and approaches used to estimate those releases; (b) the second describes the water balance and transport processes that should affect any water quality constituent considered; (c) the third discusses a solids balance and suspended solids transport, which is of principal importance in the transport of sorbed contaminants, (d) the fourth discusses transport of certain contaminants, and (e) the last two sections review the physical, chemical, and biological transformation processes for organic and inorganic contaminants in CDFs.

5. Generally, an overview of important processes is provided, as well as equations to illustrate important concepts, where appropriate. Further, the discussion and equations provide a basis for estimating the applicability of the models discussed in Part III. However, the equations presented are not intended to provide definitive engineering guidance on methods of estimation, as other methods and equations may be more appropriate for particular applications. Additional work is necessary, in some cases, to test the accuracy and practicality of some of the approaches presented.

### CDF Morphology and Characteristics

6. Confined disposal places dredged materials into a facility that normally consists of a ring dike in water or a dike extending from shore to enclose a portion of a water body as a containment area in which the material settles and consolidates. Confined disposal facilities are essentially continuous-flow treatment facilities for solids removal and retention that discharge water and some solids. The facilities may be upland or nearshore, or placed in open lake or estuarine waters. It is possible to construct these facilities in open coastal waters, in large rivers, and in the backwaters of dammed rivers. However, waves, swift currents, and limited space for navigation generally preclude construction in all locations except lakes and estuaries where currents and waves are not severe and where adequate space is available. Some in-water structures are attached to land; for these, the

original shore serves as one side of the CDF. In open water, CDF construction is generally limited to relatively shallow areas (maximum depth approximately 8 m) with the resulting emergent islands protected from erosion induced by waves and currents (Herbich 1981).

7. The general morphology of CDFs (shape in the plan view) is highly variable. Particular design and operational constraints have resulted in a wide variety of CDF shapes and sizes. This is significant in that it suggests that, while the basic processes (as described below) remain similar, any generalized assessment technique should have the capability of evaluating a wide variety of physical and operational conditions that result from the different shapes.

8. The active life of a CDF may be subdivided into three relatively distinct periods: operating, nonoperating, and filled. During the operating phase dredged material is actively discharged into the CDF, and processes associated with that disposal may largely control the quality and magnitude of releases. For example, effluent quality may be controlled more by influent quality than biological or chemical processes occurring within the CDF where discharges occur directly, such as over a weir. For most of the life of a typical CDF, no disposal operation is taking place (e.g., between filling operations, during nonoperating conditions, or following the filling of a CDF). During nonoperating conditions, discharges of contaminants may be dominated by processes such as hydraulic pumping of lake water through the dike for in-water CDFs or groundwater transport. During the final stage of operation, the CDF is essentially an extension of the shoreline or an island in which the migration and fate of contaminants are controlled by biological activity and porous media geochemistry and transport. This final stage is sometimes not fully achieved, as some CDFs are never completely filled (Marquenie, Simmers, and Kay 1987).

#### Water Balance

9. Confined disposal facilities are generally not constructed to allow water storage over a disposal cycle; therefore, inflows to a CDF must be discharged by some mechanism. Evaporation, seepage, or direct discharges over a weir or through a pump are the typical means by which water leaves the CDF. To assess discharges of the fraction of contaminants dissolved in the water, the water balance of a CDF must be known. Also, for contaminants associated

with particulates, the loadings and releases of suspended solids must be estimated, as discussed in the following section.

10. The important components of the water balance are

$$V_I + V_D + V_P + V_L = V_E + V_{SD} + V_{SG} + V_w + V_p \quad (1)$$

where

$V_I$  = initial volume of water contained inside the dikes and within the dike pores that may be displaced by dredged solids

$V_D$  = volume of water contained in the dredged material placed in the facility

$V_P$  = volume of precipitation

$V_L$  = volume of lake water transported through the dike

$V_E$  = volume of evaporation

$V_{SD}$  = volume of seepage through the dike

$V_{SG}$  = volume of seepage into or out of the groundwater

$V_p$  = volume of water remaining in the pores of the dredged materials in the facility

11. The initial volume of water may be computed from the final design for the CDF. The volume of water and solids (to estimate displacement) associated with dredged material can also be obtained from design calculations. Volumes of precipitation and evaporation can be estimated from data available from the National Weather Service. Seepage volumes must be estimated from the properties of the dikes and water elevation at the site. These rates and the pumping or discharge rates over weirs may be estimated as part of the design. The volume of water associated with the dredged materials is estimated from the sediment properties and the type of dredging equipment used. The following sections describe some formulations that have been used to determine the volumetric loadings and discharges of both water and suspended solids during and between dredging operations.

#### Water disposal rate

12. The water disposal rate during active dredging operations depends upon the volume of material dredged and the site water-sediment ratio, as illustrated by

$$Q_d = RV_{sed}/T \quad (2)$$

where

$Q_d$  = rate of water inflow from dredged material,  $m^3/day$

$R$  = water-sediment ratio of the dredged material slurry

$V_{sed}$  = in-place volume of sediment,  $m^3$

$T$  = period of time required to dredge and dispose of the volume of dredged material ( $V_{sed}$ ), day

The water-sediment ratio ( $R$ , volume of water in the slurry divided by the in-site total volume) varies with the in situ characteristics of the sediment and the type of dredging operation. For example, hydraulic dredging involves suction of sediment and relatively large volumes of water through a cutterhead placed on the bottom. Typically, one part sediment is mixed with 3 to 10 parts water to dilute the sediments.

13. Mechanical dredging involves less dilution of dredged materials. A clamshell dredge or scoop is used to pick up bottom sediments. This method involves collection of relatively smaller volumes of dredged materials compared with those collected by hydraulic dredging. The  $R$  factor in Equation 2 for mechanical dredging and disposal is the in situ water content of the sediment. Thus, mechanical unloading of mechanically dredged material from barges or scows can reduce the amount of additional dilution that would occur from hydraulic dredging and disposal. In addition, the use of slides during mechanical disposal can assist in the placement of contaminated materials and minimize mixing in the CDF.

14. Alternatively, mechanically dredged material may be transferred via pipeline by adding water to slurry the sediment. Hydraulic pumping of these materials would subject them to the same intensive mixing as would occur in hydraulic dredging.

#### Precipitation and surface seepage/runoff

15. Precipitation may be of particular importance between filling operations and following closure of the CDF. Between filling operations, precipitation on the CDF pond or exposed dredged materials can effect contaminant transport. For those CDFs that are closed, the amount of seepage expected from a CDF is directly related to the effectiveness of the cap and cover in preventing rainwater from coming in contact with the contaminated dredged

materials. Water that penetrates the cap following closure or contacts exposed dredged materials between filling operations will produce a hydrostatic gradient that will assist the migration of contaminants through the dike walls. In addition, runoff can result in solids and contaminant loadings to the pond waters. The assessment of runoff and seepage requires the availability of techniques to estimate drainage from and percolation through the exposed dredged materials or cap and cover. Models that are available for these estimates are discussed in Part III. Precipitation rates are generally available from the National Weather Service.

#### Direct discharges

16. For the purposes of this report, the discussion of discharges and seepage from CDFs is subdivided into two components: direct discharges (e.g., pumping or over a weir) and indirect discharges (such as through porous dikes or filter media or through the bottom of the site).

17. Direct discharges may occur over a weir or through direct pumping. Assuming that a CDF does not have significant water storage capacity, the discharges will be equal to the inflow plus the water displaced, as illustrated below (see Environmental Laboratory 1987)

$$Q_o = [B(1 - M) V_{sed}/T] + Q_d + Q_p \quad (3)$$

where

$Q_o$  = outflow discharge,  $m^3/sec$

$B$  = bulking factor between in situ sediment volume and settled dredged material volume above pond water level at start of disposal

$M$  = mounding factor representing the fraction of dredged material mound above pond water level during disposal

$Q_p$  = precipitation,  $m^3/sec$

18. The first term on the right-hand side (RHS) of Equation 3 represents the discharge due to displaced water resulting from solids loading. This would be applicable for an in-water CDF that initially contains water. The estimation of discharges due to displacement is dependent upon methods to estimate the bulking and mounding of the disposed solids; estimation of the discharges is discussed in the section on suspended solids transport (see paragraphs 41-74). The discharges may also be facilitated by surface trenching after the ponded surface water has been removed, as described by

Haliburton (1978). The remaining terms on the RHS represent the liquid portion of the disposal (Equation 3) and inflow from precipitation.

19. Equation 3 may be used to predict total losses from the CDF but provides little information about what specific route the discharges take, such as over a weir, through the dike, or through groundwater flows. For cases in which there are several potential discharge pathways, it may be necessary to consider alternative formulations to predict, or evaluate the relative importance of, discharge pathways. The prediction of discharge may also be of utility where time-scale fluctuations during filling are of importance. Several predictive methods or formulations are described below, including estimation of discharges over a weir or through seepage. The formulations generally require the estimation of water surface elevations within the dike (pond water or saturated surface) and in the surrounding water body in order to compute the hydraulic driving forces.

20. Weir discharges. Where a weir is present, discharges are a function of the weir characteristics and the hydraulic head difference, as demonstrated by

$$Q_o = P_w Z H^b \quad (4)$$

where

$P_w$  = weir coefficient characteristic of flow conditions over the weir, m/sec

$Z$  = weir crest length, m

$H$  = head difference between the height of the weir crest and the CDF pond, m

$b$  = empirical coefficient, dimensionless

The hydraulic head is a time-variable function of the CDF morphology and the water balance. The head difference may often be controlled by altering the weir height in order to facilitate control of solids in releases.

21. Weir coefficients are available for all standard weirs and many special-purpose weirs. French (1985) lists coefficients for most standard weirs, as does ASME (1959) and Rantz et al. 1981. McCutcheon (1988) compiles the most extensive list of weir equations and coefficients.

22. Pumping. Direct discharges may also occur via active pumping. Pumping may occur in order to direct discharges to less environmentally

sensitive areas or to treatment facilities. Pumping rates may be designed to minimize hydraulic head differences so as to reduce losses due to seepage or other mechanisms.

23. Other dewatering methods. The dewatering of upland CDFs can, in some cases, be facilitated by gravity or vacuum-assisted underdrainage. These methods are discussed in detail by Haliburton (1978).

24. Evaporation. Evaporation removes water from a CDF and should be considered in a CDF's water balance. Pan evaporation rates are generally available from the National Oceanic and Atmospheric Administration. The pan evaporation data generally overestimate evaporation expected from a CDF and must be adjusted. The evaporative loss from shallow ponds and wet soils is estimated as approximately 70 percent of the pan evaporation (US Army Engineer District (USAED), Chicago 1987). Haliburton (1978) discussed water losses due to evaporation from upland CDFs and provided summaries of mean monthly pan evaporation data for the United States for the period 1931 to 1960.

25. Evaporation is generally assumed not to remove contaminants from a water body. Losses of volatile materials are discussed in the section Suspended Solids Transport and Solids/Water Quality Interactions (see paragraphs 44-75).

#### Indirect discharges

26. Indirect discharges, as discussed here, refer to discharges through some media which may alter the transport characteristics of the contaminant. For example, discharges through a porous dike may remove solids via filtration and contaminants through sorption. Indirect discharges may occur principally through dike or groundwater seepage.

27. Dike seepage. Seepage losses through a saturated porous dike are a function of the hydraulic conductivity of the dike or filter material and the hydraulic head. For example, discharges due to seepage through the dike wall may be estimated from the seepage velocity ( $V_s$ )

$$Q_s = V_s A \quad (5)$$

where

$Q_s$  = seepage flow,  $m^3/sec$

$A$  = cross-sectional area of the saturated portion of the dike,  $m^2$

28. The seepage velocity may be estimated from

$$v_s = \frac{K}{n} \left( \frac{\Delta H}{L} \right) \quad (6)$$

where

$K$  = hydraulic conductivity, m/sec

$n$  = porosity, dimensionless

$\Delta H/L$  = hydraulic slope, dimensionless

If the saturated area ( $A$ ) of the dike through which flow occurs can be considered the product of the arithmetic average of the time-varying head between the interior pond ( $H_i$ ) and exterior ( $H_o$ ) water surface  $[(H_i + H_o)/2]$  multiplied by the length of the dike's inner perimeter, Equation 5 may be reexpressed as

$$Q_s = \frac{KW}{2nL} (H_i^2 - H_o^2) \quad (7)$$

where  $W$  is the length of the inner dike perimeter, in meters.

29. The hydraulic conductivity of the material refers to the ease with which a fluid can be transported through a saturated porous medium. It is a function of the characteristics of the porous medium and the fluid. Where a dike is constructed as a series of materials of differing hydraulic conductivity, such as where a filter liner is used, seepage may be computed from an effective (or equivalent) conductivity of the dike. The equivalent conductance ( $S_{eq}$ ) may be considered a series conductance problem where the equivalent conductance is the product of the individual conductance values over their sum, or

$$S_{eq} = \frac{\prod_{i=1}^N K_i \frac{A_i}{L_i}}{\sum_{i=1}^N K_i \frac{A_i}{L_i}} \quad (8)$$

where

$N$  = number of conductance intervals

$i$  = conductance interval index

30. Following closure of the CDF, the amount of seepage expected from a CDF is directly related to the effectiveness of the cap and cover. Water that penetrates the cap will produce a hydrostatic gradient. Therefore, assessment of postclosure seepage requires the availability of techniques to estimate drainage from and percolation through the design cap and cover.

31. Groundwater flows. The impact of seepage on groundwaters may vary with CDF structures. For in-water CDFs with porous dikes, the Environmental Laboratory (1987) assumed that the hydraulic gradient driving bottom seepage was small and further retarded by consolidated solids, making bottom seepage small relative to other discharge mechanisms. Where the porosity of a dike is limited and the hydrostatic head not controlled, significant discharges to groundwater flows may occur.

32. For the case of upland CDFs, the discharges to groundwater would be impacted by the location of geosynthetic or natural barriers to seepage. Flows through the unsaturated, or vadose zone, are impacted by different processes than through saturated media and require different methods for estimation of their magnitudes. Techniques are available to estimate vadose zone transport, which varies with soil permeability, soil water characteristics (relationship between water content and hydraulic conductivity), and the degree of homogeneity of the soils. Available techniques to estimate flows through the saturated and vadose zones are discussed in Part III.

33. Hydraulic pumping and wave mixing. Discharges can occur through the porous dike of in-water CDFs due to variations in the water surface elevations of the surrounding water body. This mechanism is referred to as hydraulic pumping and results from variations in the hydraulic slope between the dike interior and the containing water body. Near-field mixing at the outside edge of the dike and extending into the porous dikes can also be important. Near-field mixing may reduce exposure concentrations. The near-field mixing is a function of local wind speed and direction, bathymetry, other nearby structures, wave action, and the characteristics of the dike.

34. Contaminant releases due to hydraulic pumping are known to occur in some systems and would be expected in CDFs. However, methods to predict those releases are poorly developed.

35. A number of studies have been conducted to estimate wave transmission and reflection at permeable breakwaters, primarily to evaluate the effectiveness of alternative breakwater configurations. Sollitt and Cross (1976) reviewed available methods and derived theoretical relationships to estimate

transmission and reflection of nonbreaking waves from rubble breakwaters, and compared their predictions to experimental results. Madson and White (1976) and Madson, Shusang, and Hanson (1978) refined theoretical methods for predicting transmission through breakwaters.

36. Factors influencing reflection and transmission through porous dikes are illustrated by

$$v_w = \frac{g}{h^{0.5}} a_i \quad (9)$$

$$v_r = v_w \frac{w}{w + \frac{2n}{kwf}} \quad (10)$$

$$v_t = v_w \frac{w}{w + \frac{kwf}{2n}} \quad (11)$$

where

- $v_w$  = wave incident velocity, m/sec
- $g$  = gravitational acceleration,  $m/sec^2$
- $h$  = mean water depth, m
- $a_i$  = incident wave amplitude, m
- $k$  = wave number,  $1/m$
- $w$  = width of the structure, m
- $f$  = friction factor, dimensionless
- $v_t$  = transmitted velocity, m/sec
- $n$  = porosity, dimensionless

37. Since the wave number ( $2\pi/L$ , where  $L$  is the wave length) is inversely proportional to the wave length, the above formulation demonstrates that wave transmission decreases with decreasing wavelength. The amounts transmitted and reflected are also affected by dike characteristics, such as width, length, and porosity as well as factors influencing friction losses, such as the hydraulic properties of the dike.

38. Formulations of this type may provide a means of estimating a transmission coefficient, which may then be of use in estimating dike

exchanges. Additionally, the reflection coefficients could be used to estimate mixing zones. However, additional development and testing are required to fully develop methods that may have good predictive capability.

39. In addition to nonbreaking waves, breaking waves can contribute to near-field mixing in the area of the dike face and contaminant exchanges. An active swash zone of wave runup on the outside of the dike can involve very active mixing on the outer dike face. Here the energy is sufficiently high to quickly mix any contaminant migrating to the outer face.

40. Longuet-Higgins (1983) also demonstrates in an interesting experiment that seaward pulses at the toe of a beach are set up by shorter period waves. Here the waves that have a period or length scale (distance from trough to trough) similar to the length of the beach face on the dike cause a circulation cell that pushes water into the upper part of the dike and water from the interior out of the toe of the dike. These circulation cells are controlled by wave period, beach slope, and porosity. However, the exact effect is not well understood.

#### Solids Balance

##### Suspended solids transport and solids/water quality interactions

41. The design of CDFs focuses on controlling the loss of solids because of their association with contaminants. The importance of this association with particulates was recognized in the executive summary of the Corps of Engineers' Dredged Material Research Program (Saucier et al. 1978).

If a confined disposal facility is to be effective from an environmental protection standpoint, it must be efficient in retaining a high percentage of the finer soil particles, for it is these clays and silts that carry the contaminants.

Because of the interaction between solids and contaminants, an assessment of suspended solids transport is required to estimate the environmental effects of CDFs. Recent experience at the USEPA Environmental Research Laboratory, Athens, GA, clearly demonstrates that the neglect of solids transport and partitioning makes it very difficult to understand the ultimate fate of sorbed contaminants. It should be noted that partitioning between deposited and suspended sediments and small amounts of dissolved material can be very dynamic. The fact that 90 to 99 percent of some hydrophobic contaminants is

associated with solids should not be taken to infer that partitioning is a static process in which solids interactions are not important. More informative and useful is the concept that solids with highly hydrophobic contaminants function as a capacitor to maintain dissolved concentrations at relatively constant concentrations until dilution with clean sediments or extremely large quantities of water (on the order of  $10^6$  for typical hydrophobic chemicals) occurs. Therefore, suspended dredged solids have overriding importance in determining the fate of hydrophobic contaminants.

42. Suspended solids transport, as discussed here, includes processes such as:

- a. Dilution with water during dredging and transport (if a slurry pipeline is used).
- b. Degree of mixing during dredging, transport, and placement in the CDF.
- c. Degree of mixing of contaminated and uncontaminated sediments in the CDF.
- d. Settling efficiency and type of settling.
- e. Compaction in the bed.
- f. Erosion and resuspension into the water column.
- g. Transport out of the CDF.

The characteristics of disposed dredged materials are expected to change with time, which may affect their toxicity (Simmers, Richards, and Piku 1986) and transport characteristics.

43. A material balance for solids can be written, similar to that previously described for water. The major components of the solids balance include loadings and discharges. Also of importance are the rates of interaction between the materials deposited in the benthic or bed layers and the overlying water column within the CDF.

#### Solids inflows and loadings

44. The amount of dredged material placed in a CDF can be estimated from in situ sediment characteristics. The amount of solids placed in the CDF per day is

$$L_s = \frac{SV_{sed}}{T} \quad (12)$$

where

$L_s$  = solids load, kg/day

$S$  = in situ sediment concentration, kg/m<sup>3</sup>

The in situ sediment concentration may be estimated from the sediment density and porosity as

$$S = 1,000 \ell/m^3 (1 - n) \rho_s \quad (13)$$

where

$n$  = in situ sediment porosity

$\rho_s$  = sediment density, kg/ℓ

45. For saturated sediments, the porosity is equal to the volumetric water content. In situ porosity and density, as well as contaminant concentration, can be expected to vary spatially. To some extent, spatial variability will be offset by mixing of sediments during dredging, transport to the CDF, and placement. However, when mixing is not extensive, it may be necessary to sample batches of sediment during placement to quantify precisely the sediment and contaminant mass going into the CDF; otherwise, it will be necessary to accurately map in situ characteristics and statistically estimate mean concentrations and the uncertainty or variability about the mean. In either case, measurements of the exact mass placed in the CDF are necessary for precise estimates of migration.

46. The varying sediment characteristics may allow dredging operations to be managed in order to minimize the environmental impact of the associated contaminants. For example, dredging operations may be designed to concentrate on areas of different degrees of contamination at different times. Dredging relatively clean sediments and covering previously disposed contaminated sediments with these sediments may aid in controlling pond water contaminant concentrations.

#### Solids production in the CDF

47. Solids may also be produced in CDFs. Generally, dredged materials are rich in phosphorus (which can be mobilized by in situ reducing conditions) and nitrogen. These nutrients trigger excessive algae growth that converts dissolved nutrients to particulate organic matter. By comparison, the solids produced by primary productivity are a very small fraction of the solids placed in CDF. However, these solids can be important if the amount present

reaches levels comparable to the amount of organic carbon associated with the dredged material in the CDF. Algae and other detritus should be considered as a concentrated sponge for sedimentary contaminants. In addition, these organic materials are the base of the food chain that can bioaccumulate contaminants.

48. The amount of solids production can be crudely approximated from the amounts of nutrients available. Nutrients are typically measured in an elutriate test or can be estimated from in situ concentrations of nutrients if these are adequately measured. More precise estimates of solids production can be derived from eutrophication models that take into account light and nutrient limitations on algae growth.

#### Solids losses

49. Solids are lost from CDFs in two primary ways. First, and by far the most important for CDF design, are direct losses where suspended sediment is washed out of the facility with excess water flowing over the weir or being pumped out. Second, fine sediments can be lost indirectly by being washed through porous dikes. The second transport mechanism was a special concern with early CDF designs that did not adequately attempt to control all solids. More recent design methods attempt to avoid all uncontrolled solids released through the dike walls.

50. Indirect losses. Discharges through the dike should be expected where there is a positive hydrostatic gradient between the CDF pond and the water surface elevation of the containing water body. However, depending upon the dike characteristics, the solids associated with these discharges should be partially or completely removed from the indirect discharges via filtration. An estimation of the solid removal via filtration may be obtained by the formula given below (Krizek, Fitzpatrick, and Atmatzidid 1976).

$$S = S_o \exp (-F_c W_f) \quad (14)$$

where

- S = solids concentration passing through dike, mg/l
- S<sub>o</sub> = solids concentration in CDF pond, mg/l
- F<sub>c</sub> = filter coefficient, m<sup>-1</sup>
- W<sub>f</sub> = width of dike filter, m

51. The filter coefficient can be estimated from

$$F_c = 0.4D_{10}^{-1.84} \quad (15)$$

where  $D_{10}$  is the effective size of the dike particles (millimeters). The effective size of the filter media would be expected to vary as the filter becomes clogged with dredged materials.

52. The USAED, Chicago (1987), used Equations 14 and 15 to estimate the efficiency of a filter of lake sand, with mean particle size of 0.08 mm, for a proposed CDF in Waukegan Harbor. They indicated that the filter efficiency of 1 ft (0.3048 m) of sand was  $3.0 \times 10^{-6}$ , indicating that 99.9997 percent of the suspended solids would be removed within the first foot of a sand filter. This would suggest that control of indirect discharges of solids through the dike may be obtained with dike designs that incorporate filtration. The Chicago District also considered variations in filtration efficiencies with time as filters became clogged in their modeling studies.

53. Direct discharges. Direct discharges of solids can occur over weirs or through direct removal via pumping. The amount of solids removed is dependent on the discharge rates and the suspended solids concentration. The concentration of suspended solids in the discharge is dependent upon the mixing of dredged materials during placement, initial sedimentation, and resuspension during and immediately following filling. The suspended solids concentrations will be a function of the transfer technique and the degree of dilution occurring. For example, dredged material placement using slides or placement onto existing mounds would be expected to result in lower suspended solids concentrations than direct discharges into open water.

54. The direct discharges may be treated further where necessary to control contaminant releases. Small cells can be added to the CDF to achieve chemical mixing of coagulates and settling or additional filtration. In addition, the waste effluent can be routed into the local sewerage system for treatment at the local wastewater treatment plant.

#### Solids/water interactions

55. For CDF water quality assessment purposes, suspended solids are of primary interest in estimating discharges and exposure concentrations, with

the finer fractions of materials (silts, clays, organic detritus, and live plankton materials) having most importance.

56. Solids/water interactions will vary during the operational stages of a CDF. During dredging and transferal of dredged materials, mixing is expected to be intensive, particularly if the materials are hydraulically dredged. Transfer into the CDF via hydraulic pumping would subject the dredged materials to the same intensive mixing and dilution as would occur in hydraulic dredging. Hydraulic pumping or disposal requires large volumes of water to slurry the sediments. The mechanical placement of dredged materials can reduce the amount of additional dilution that would occur from hydraulic transfer. Mixing during mechanical placement could be further retarded when a metal slide is used to allow the dredged material to gently flow to the bottom as a density underflow.

57. Disposal will be followed by initial sedimentation, which may occur as either discrete particle settling or flocculent or zone settling. Following initial sedimentation, solids/water interactions are influenced by the size, shape, density, and surface area of the particles as well as the surface physical and chemical properties, including electric charge. A review of particle composition, behavior, and interaction with water density was given by Lal (1977). Confined disposal facilities are expected to act as a primary settling basin, and following initial settling the suspended solids concentrations will depend upon the interactions between the water column and the surficial layers of disposed dredged materials.

58. Settling and deposition. After disposal, any suspended particles will begin to settle. Initially, sedimentation may involve discrete particle settling (Type I); flocculent settling (Type II), where particles coalesce or flocculate and change settling velocity during settling; and zone settling (Type III), where particle forces retard settling and cause the material to settle largely as a unit, or combinations thereof. The particle concentration, size, shape, density, surface area, and surface charge, among other characteristics, determine which settling regime dominates. See the review by Lal (1977).

59. A CDF is expected to act as a primary settling basin. Sand and large discrete noncohesive particles will tend to settle and form a fan of coarse material at the point of introduction. Flocculent or zone settling may be the dominant form of settling for the remaining particles. The settling behavior of dredged material solids has been described by Montgomery (1978,

1979), Montgomery, Thackston, and Parker (1983), and Palermo and Thackston (1988a,b).

60. Between filling operations, materials are expected to be resuspended by wind and to settle. There are indications that resuspension and deposition will reach a long-term balance to maintain an average suspended concentration. In the Chicago District CDF, this average was approximately 100 mg/l. Long-term deposition to maintain this balance is expected to chiefly involve discrete particle settling of dredged materials as well as solids produced in the CDF (i.e., algal cells).

61. These particle settling velocities can be quite variable depending on the regime. As a result, the contaminant migration rates from the water column to the bed can be equally variable.

62. For discrete particle settling, the settling velocity is a function of Brownian motion, turbulent diffusion, and fall velocities. Brownian motion is negligible for most particles of interest. Settling velocities are functions of size, shape (drag coefficient), and density and can be reasonably well predicted for larger mineral particles (Dietrich 1982; Gibbs, Matthews, and Link 1971). For micron-size and smaller particles, and particularly for organic particles, the large diversity in sizes, shapes, and density (Ives 1973, Lal 1977) often requires indirect determinations of fall velocities from settling traps or mass balances. Discrete particle settling velocities ( $w_s$ , in centimeters per second) can be estimated from Stoke's law, which is

$$w_s = \frac{gd^2}{18\mu} (\rho_p - \rho_f) \quad (16)$$

where

$g$  = gravitational acceleration, m/sec<sup>2</sup>

$d$  = particle diameter, cm

$\mu$  = dynamic viscosity of the fluid, g/cm-sec

$\rho_p$  = particle density, g/cm<sup>3</sup>

$\rho_f$  = fluid density, g/cm<sup>3</sup>

The silts and clays carrying pollutants typically range in diameter from 0.002 to 0.02 mm, with densities of 2 to 2.7 g/cm<sup>3</sup>. Stoke's law is valid for Reynolds numbers ( $Re = \rho_f w_s d / \mu$ ) less than about 0.1.

63. For dredged material disposal, with suspended solids concentrations averaging approximately 145 g/l, particles general do not settle as discrete units. At these high concentrations, sedimentation occurs as either flocculent or zone settling processes (Montgomery, Thackston, and Parker 1983), or a combination of those processes.

64. Collisions between small cohesive particles tend to lead to coagulation and the formation of flocs. Flocculation rates are dependent upon the size distribution and relative composition of the clays and electrolytes and upon local boundary shear stresses (Mills et al. 1985) as well as salinity. Turbulence increases the collisions while salinity increases the cohesion between particles (Sheng 1983). The effective density of the floc may vary considerably from that of the individual particles, making prediction of settling velocities difficult (Stefan, Ambrose, and Dortch 1988).

65. Zone settling usually occurs at high solids concentrations, such as those characteristic of dredged materials. Under zone settling, particles may become entrapped in a loose, open matrix that settles as a unit.

66. The mathematical formulation of predictive equations for flocculent or zone settling velocities is difficult. However, laboratory column settling tests have been developed to provide estimates of suspended solids concentrations and settling rates in order to estimate effluent suspended solids and the required storage capacity for CDFs. Montgomery (1978, 1979) and Montgomery, Thackston, and Parker (1983) described column settling tests for dredged materials and provided guidance on the sampling and laboratory testing required. Flocculent and zone settling tests were developed to determine settling velocities, and design procedures were recommended. Palermo and Thackston (1988a,b) described a refined test for zone settling that can be used to estimate the suspended solids concentrations in the clarified supernatant and to estimate suspended solids in the effluent following disposal. The method was tested against field data from five sites, including fresh and saltwater environments.

67. Solids removal from the water column can be enhanced by physical and chemical processes commonly used in treatment operations. Physical mechanisms include adsorption. Chemical processes include precipitation and coagulation.

68. Resuspension and scour. The resuspension or entrainment of solids in a CDF is primarily a function of settled material properties and shear at the solids-water interface. The primary source of shear is wind at the

surface. Generally, there is a critical shear stress for the mobilization of different types of sediments under different conditions in the bed.

69. Noncohesive sand and silt have a well-defined critical shear stress that controls resuspension. Once the critical stress is exceeded, particles are entrained until the capacity of the flow to carry the material is exceeded (which changes as the material is entrained and causes stratification of the flow) or until the material at the interface is exhausted and no longer available for entrainment (bedrock or highly compacted layers are reached). The material stress or yield stress of sands and silts is not affected very much by compaction and other bed processes. Therefore, a constant critical stress is normally applicable for layers of sand in which the size distribution and particle shapes do not change. However, these particles are typically unimportant in transporting and binding contaminants.

70. The entrainment of cohesive particles such as clays and organic materials is different in at least one important aspect. In addition to being the dominant carrier of sorbed contaminants, these particles undergo changes in critical shear stress in the bed as compaction and biogeochemical changes (i.e., variations in salinity, pH, irrigation of the bed by microfauna, organic content, etc.) occur. (See Sheng (1983) regarding the time-history of bed changes.) Also fine-grained cohesive sediments tend to have smooth plane beds contrasted to ripples and dunes for some flows over noncohesive particle beds. As a result, flows over cohesive sediments tend to be better behaved; they are typically a smooth boundary (or transition) turbulent flow compared to a rough turbulent flow over wavy sand beds. Furthermore, the entrainment of cohesive materials increases the viscous sublayer faster than the entrainment of noncohesive materials. The enhanced viscous sublayer causes the flow to be a smooth boundary type as well.

71. Since flows over cohesive beds tend to be better behaved, observations typically refer to entrainment as mass erosion or as peeling the bed, layer by layer, in any orderly manner (Lick, Ziegler, and Tsai 1987). Mass erosion continues until highly compacted bed layers are exposed where the critical stress exceeds the fluid shear stress. By contrast, entrainment of sands on wavy beds tends to be chaotic. Turbulent structures in a rough boundary flow form at bed level, usually in a horseshoe shape over three-dimensional dune structures that violently entrain particles and inject them, as a jet, higher into the flow or into a saltation trajectory where the grain rolls on the bed or quickly falls back to the bed.

72. The critical shear stress of a cohesive layer in the bed can be quite variable depending on when the layer was deposited, how deeply it was buried, and to what salinities and other geochemical changes it has been exposed. Freshly deposited material at the base of a hindered settling zone will be entrained by very small shear rates. By contrast, the same sediments can be deeply buried for a long period of time in high-salinity water, and the resulting tightly compacted bed will have a very high critical shear stress. As a result, it is not always immediately clear that a particular cohesive sediment has a critical shear stress since the stress is variable.

73. In addition to wind shear, bioturbation can cause significant resuspension. Methods of simulation are approximate, but reasonable calculations are possible when the type and density of organisms are known. Gschwend et al. (1986) compiled the data available for turnover rates for the main two types of bioturbation: ploughing and conveyor belt. They also reviewed the best formulations for both types and presented example calculations that included contaminant flux. Generally, site-specific studies are required to establish entrainment rates.

74. Consolidation/desiccation. The consolidation and desiccation of disposed solids are of importance from water quality and design perspectives. Contaminants may be released during the consolidation processes, and subsequently, the desiccation processes will alter the surface characteristics of the bottom solids. Consolidation will also impact the water released from the dredged materials as well as their volumes, which in turn affect water releases through the impact on hydraulic driving forces. Processes impacting consolidation and desiccation are discussed by Johnson (1976), Haliburton (1978), and Cargill (1985).

#### Contaminant Transport

75. Contaminant transport and its resulting mass loadings and exposure concentrations may be estimated for some materials by assuming that they act conservatively; that is, they do not degrade and are not produced as a result of other interactions. However, for the case of some toxicants, such as ammonia, production from the degradation of organics in anaerobic environments must be considered, particularly during nonoperating conditions. For hydrophobic materials, such as polychlorinated biphenyls (PCBs), and many heavy metals that interact strongly with solids, estimation of that

association is necessary to determine their mobility. This section briefly describes some of the factors affecting transport, and is followed by a discussion of contaminant sorption and transformations.

76. Contaminants are transported by both the water mass and, for sorbed contaminants, the solids mass, as described above. However, transport is affected by the distribution of contaminant mass among solid and liquid phases as well as processes that transform the contaminant. This section describes some of the processes impacting contaminant transport.

#### Loadings

77. Contaminant loadings to a CDF occur principally from the dredged material and include the contaminant associated with the water mass as well as, for sorbed contaminants, the solids mass. Contaminant loadings are influenced by dredging operations, the characteristics of the dredged material, and the partitioning relationships between the contaminant and solids.

78. Contaminant loadings are the sum of the particulate and dissolved loadings--the product of their loading rates and their associated contaminant concentrations. However, for sorbed contaminants, these loadings are not independent. That is, as the dissolved concentrations are diluted during dredging, additional contaminants may be desorbed. McCutcheon, Ambrose, and Martin (1988) indicated that, assuming equilibrium partitioning and reasonable ranges of partitioning, the contaminated sediments in the dredged material would have to be diluted by a factor of  $10^6$  before significant reductions in dissolved concentrations would occur.

79. The distribution of contaminants among dissolved and particulate phases may be influenced by sorption kinetics. The potential effects of sorption kinetics are described further in the subsection on sorption/partitioning (see paragraphs 93-102). However, kinetic limitations, involved when PCBs and some other organic contaminants desorb from complex aggregates of fine particles, are not expected when sediments are pumped and jetted into the CDF. The intense mixing in the pipeline from the dredge to the barge, and from barge to CDF, is expected to accelerate desorption due to the breaking down of particle aggregates.

80. The effects of contaminant loadings are impacted by the placement of the dredged materials. The properties of the deposited dredged materials would also be expected to change following exposure due to mounding. The effects of placement of dredged materials on exposed sediments would be expected to result in different effects than those placed in open water.

## Discharges

81. Direct discharges. Total contaminant direct discharges are the sum of the particulate and dissolved concentrations multiplied by the discharge rate. However, those concentrations are affected by a number of processes, including solids/water interactions and contaminant transformations, as discussed in later sections.

82. Dike seepage/groundwater transport. Indirect discharges due to seepage or groundwater flow are affected by sorption and contaminant transformations.

83. Sorption directly impacts the losses of contaminants due to indirect discharges, both through advective and diffusive transport. The effect of partitioning is essentially to retard the contaminant transport. The effect of partitioning on transport rates may be demonstrated by comparing the transport velocity of water through porous media to that of contaminants (McCutcheon, Ambrose, and Martin 1988),

$$V_c = f_d v_w \quad (17)$$

where

$v_c$  = velocity of contaminant in porous media, m/day

$f_d$  = fraction dissolved, dimensionless

$v_w$  = water velocity in porous media, m/day

Therefore, as the partition coefficient is increased, the velocity of the contaminant, and its resulting penetration through the dike, decreases. Essentially, more water flow is required to move a given mass of a contaminant through the dike as the partition coefficient increases. The result of this effect may be to reduce releases or to distribute releases over longer time frames.

84. Alternatively, the effect of partitioning on indirect discharges may be illustrated by considering a square-wave of material moving through a homogeneous dike. For this case, the loading to the water column (due to advection alone) can be estimated from

$$L = C_d \left( Q_w T - \frac{V_d}{f_d} \right) \quad \text{for } Q_w T > \frac{V_d}{f_d}$$

and (18)

$$L = 0 \quad \text{for } Q_w T \leq \frac{V_d}{f_d}$$

where

$L$  = total loading, mg

$C_d$  = dissolved concentration, mg/m<sup>3</sup>

$Q_w$  = water flow, m<sup>3</sup>/day

$T$  = flow duration, day

$V_d$  = volume of the dike, m<sup>3</sup>

This simply states that a homogeneous dike should have some storage capacity (approximately  $V_d/f_d$ ) for a material that sorbs and that no loadings from the dike would be expected until after that capacity has been depleted. While an oversimplification, this illustrates the effects that sorption may have on transport through porous media.

#### Solids interactions

85. The interaction between particles and water chemistry becomes particularly complex near the bed because of (a) strong vertical velocity gradients associated with shear forces, (b) activities of organisms such as those associated with biofilms, invertebrates, crustaceans and fish, and (c) pore water movement into and out of the outlying waters. Microcosm models or measurements of these systems are necessary to provide the input or withdrawal rates of dissolved substances. Examples include sedimentary oxygen demand (Chen, Brannon, and Gunnison 1984; Gantzer et al. 1988), phosphorus release, and PCB resuspension.

86. The effect of suspended solids concentrations can be demonstrated by first examining the steady-state distribution of contaminants in a water column (layer 1) overlaying a bed (layer 2), where the distribution is affected only by resuspension and settling. At steady state, the total contaminant balance may be written as

$$V_{set}C_{s,1}S_1 = V_{res}C_{s,2}S_2 \quad (19)$$

where

$V_{set}$  = settling velocity, m/day

$C_s$  = sorbed concentration, mg/kg

$S$  = suspended and bed solids concentration, kg/l

$V_{res}$  = resuspension velocity, m/day

The suspended solids concentrations in the water and bed are related at steady state by

$$V_{set}S_1 = V_{res}S_2 \quad (20)$$

87. Substituting Equation 20 into Equation 19 and simplifying yields an equilibrium condition such that  $C_{s,1} = C_{s,2}$ . The dissolved concentration of the layers may be obtained by dividing the sorbed concentration by the partition coefficient (see Sorption/partitioning, paragraphs 93-102). If the partition coefficient is constant between the bed and water column,  $C_{d,1}$  is equal to  $C_{d,2}$  where  $C_d$  is the dissolved concentration. This implies that, for this very simplistic case, the suspended solids concentrations (if non-zero) have no impact on the dissolved concentration and the dissolved concentration in the water column will equal that in the bed pore water. The suspended solids concentration for this simplistic case affects only the total and particulate contaminant concentrations, not the dissolved or sorbed concentration per unit solid.

88. Secondly, it should be noted that the sorbed and dissolved contaminant concentrations will not be equal at steady state where other loss mechanisms in the water column occur, such as volatilization. For example, if volatilization at a constant rate (applied only to the dissolved contaminant) is added to the left side of Equation 20, the resulting steady-state concentrations would be

$$C_{s,1} = \frac{V_{set}S_1}{V_{set}S_1 + K_v/K_p} C_{s,2} \quad (21)$$

where  $K_v$  is the volatilization rate (meters/day) and  $K_p$  is a partition coefficient (here in units of cubic meters per gram). This expression does not describe the effects of losses on the sorbed concentration ( $C_{s,2}$ ), which would decrease over time in response to losses. Equation 21 suggests that, where suspended solids concentrations are in equilibrium with the water column, the effect of volatilization will appreciably reduce the sorbed concentration in the water column when  $K_v/K_p$  is larger than  $V_{set}S$ .

89. Third, the above discussion considers only conditions at steady state. However, the time to steady state is critical in determining concentrations and is directly related to the magnitude of the fluxes between the bed and water due to processes such as resuspension and settling. For example, in the presence of volatilization at low rates of bed/water column interaction, sorbed and dissolved concentrations in the water column would be expected to be quickly reduced. However, at high rates of bed/water column solids interaction, where the water column overlies contaminated deposited dredged materials, solids controls may be ineffective.

#### Diffusive exchanges

90. Diffusive exchanges can impact the releases of CDFs and the time frame over which releases may occur. Diffusive exchanges through the dike wall and between dike and the interior pond can affect concentrations and releases of contaminants. Diffusive exchange between the bed and water may be a major mechanism for transferring contaminants, particularly for nonhydrophobic materials.

#### Contaminant Transformations - Organic Chemicals

91. Synthetic organic chemicals include a wide variety of toxic materials regulated based upon threshold concentrations as well as tolerable durations and frequencies of exposure. These concentrations may be affected by transformations as well as physical transport. Many of the rates and kinetic formulations for describing these transformations were summarized by Bowie et al. (1985).

92. Transformations may be broadly defined as physical, chemical, and biological. Physical transformations include such processes as sorption or volatilization, which alter the physical state of the material without altering its chemical composition or total mass. As a result of chemical and biological transformations, chemical concentrations and resulting observed toxic effects often decline over time. The loss processes considered important for most synthetic organic chemicals include hydrolysis, photolysis, and bacterial degradation. Chemical oxidation and reduction are sometimes important as well.

Sorption/partitioning

93. Many toxic materials sorb strongly onto particulates. Estimates of sorption are required in assessing the effects of toxic material in CDFs and their releases, since processes such as transport and transformation, which impact dissolved and particulate fractions, differ.

94. Sorption is the bonding of dissolved chemicals onto solid phases ( $S_i$ ) such as benthic and suspended solids, biological material, and sometimes dissolved or colloidal organic material, as described by

$$S_i + C_d \leftrightarrow \frac{C_{si}}{n} \quad (22)$$

where

$C_d$  = dissolved chemical concentration, mg/l

$C_{si}$  = chemical concentration in the solid phase  $i$ , mg/kg

$n$  = porosity of the material

95. For environmentally relevant concentrations (less than  $10^{-5}$  M or one-half water solubility), equilibrium sorption is linear with dissolved chemical concentration (Karickhoff 1984), or

$$C_{si} = K_{pi} C_d \quad (23)$$

and  $K_{pi}$  is the sorption partition coefficient between the two phases (l/kg). At equilibrium, then, the distribution among the phases is controlled by the partition coefficients,  $K_{pi}$ . The total mass of chemical in each phase is controlled by  $K_{pi}$  and the amount of solid phase present.

96. Values for the partition coefficients can be obtained from laboratory experiments. For organic chemicals, laboratory studies have shown that the partition coefficient is related to the hydrophobicity of the chemical and the organic matter content of the solids. Normalization of the partition coefficient by the organic-carbon content of the solids has been shown to yield a coefficient,  $K_{oc}$ , that is relatively independent of other solids characteristics or geographic origin. The partition coefficient is then related to the  $K_{oc}$  by

$$K_{pi} = f_{oc,i} K_{oc} \quad (24)$$

where  $f_{oc,i}$  is the organic carbon fraction of the solid  $i$ .

97. Correlation of  $K_{oc}$  with the water solubility of the chemical or the octanol-water partition coefficient of the chemical has yielded successful predictive tools for incorporating the hydrophobicity of the chemical in an estimate of its partitioning. For example, where no  $K_{oc}$  values are available, they may be estimated using the following correlation with the octanol-water partition coefficient ( $K_{ow}$ ):

$$\log K_{oc} = a_0 + a_1 K_{ow} \quad (25)$$

where  $a_0$  is approximately  $\log(0.6)$  and  $a_1$  is on the order of 1. However, these correlations do poorly for chemicals with very low or very high hydrophobicity because of deviations from hydrophobic adsorption. Chemicals containing polar functional groups and low octanol-water partition coefficients tend to exhibit hydrophilic contributions to adsorption, whereas large non-polar molecules with high octanol-water partition coefficients generally require long time periods to reach equilibrium, resulting in low estimates of  $K_{oc}$  when sorption is measured over short time frames. The latter effect is particularly significant because it suggests that the assumption of instantaneous equilibrium used by the toxic chemical models may be invalid for those chemicals for which adsorption is the most important process.

98. A common assumption in assessing the distribution of chemicals between sorbed and dissolved phases is that these reactions are fast relative

to other environmental processes, and therefore equilibrium may be assumed. In addition to the assumption of instantaneous equilibrium, implicit is the additional assumption of reversibility. This is usually reasonable for inorganic materials, such as trace metals. However, laboratory data for very hydrophobic organic chemicals suggest that a hysteresis exists, with desorption being a much slower process than adsorption. Karickhoff suggests that this effect may be the result of intraparticle kinetics in which the chemical is slowly incorporated into components of the sorbant. This phenomenon is not well understood, and no quantitative modeling framework is available to characterize it.

99. Sorption kinetics may impact contaminant distributions in CDFs. While more than 80 percent of the sorbed phases of hydrophobic organics deposited in CDFs may desorb quickly (in less than a day), as many as 1 to 3 months may be required for chemicals such as PCBs to desorb completely from complex aggregate particles and reach equilibrium. Adsorption may occur, for example, onto dike materials or suspended solids, such as algal cells. Sorption onto sand and limestone particles is expected to reach an equilibrium quickly since it is controlled by surface phenomena rather than diffusion into complex particles. In addition, the limited sorption capacity is expected only to slow the transport of contaminants through the dike, without reducing ultimate exposure concentrations. Equilibrium sorption may not be environmentally conservative where transport is rapid in relation to the kinetics of adsorption. Therefore, the use of the equilibrium sorption assumption in estimating concentrations of organic contaminants in CDFs may result in lower predicted loadings and exposure concentrations than would actually occur if sorption were kinetically controlled.

100. At equilibrium, the total chemical ( $C_t$ ) can be expressed as the sum of its dissolved and particulate forms

$$C_t = C_d n + \sum S_i C_{s_i} \quad (26)$$

Substituting Equation 23 and rearranging yields an expression for the fraction dissolved ( $f_d$ )

$$f_d = \frac{C_d n}{C_t} = \frac{1}{1 + \sum K_{pi} \frac{S_i}{n}} \quad (27)$$

Similarly, the fraction particulate ( $f_p$ ) can be estimated from

$$f_p = \frac{\sum K_{pi} \frac{S_i}{n}}{1 + \sum K_{pi} \frac{S_i}{n}} \quad (28)$$

101. Empirical evidence has suggested that for typical water column solids concentration ( $n = 1$ ), the partition coefficient for hydrophobic organics is inversely related to the particle concentration. A particle interaction model has been proposed by Di Toro (1985) which describes this relationship. The equation defining the partition coefficient using this relationship is

$$K_{pi} = \frac{K_{pio}}{1 + \frac{S_i K_{pio}}{v_x}} \quad (29)$$

where

$K_{pio}$  = limiting partition coefficient with no particle interaction

$S_i$  = solids concentration, kg/l

$v_x$  = ratio of adsorption to particle-induced desorption rate

Di Toro found that  $v_x$  was on the order of 1 over a broad range of chemical and solids types.

102. A potential consequence of the particle interaction model for very hydrophobic organic materials (those with large partition coefficients) is that as the limiting partition coefficient increases, the water column partition coefficient ( $K_{pi}$ ) approaches  $v_x/S_i$ . When this is substituted into the expression for the dissolved fraction (Equation 27), assuming that  $v_x = 1$ , it can be demonstrated that the dissolved fraction will approach 0.5.

$$f_p = \frac{1}{1 + \frac{S_i}{S_1}} = 0.5 \quad (30)$$

### Ionization

103. Ionization is the dissociation of a chemical into multiple-charged species. Ionization can be important because of the different toxicological and chemical properties of the unionized and ionized species. Consider a weak acid  $AH_3$  or base  $BH_3$ , which may or may not react with water molecules to form charged anions and cations (ionize):



These reactions are rapid. At equilibrium, the distribution of chemicals between the unionized and ionized species is controlled by the pH of the water and ionization constants.

104. Stronger acids and bases may undergo further ionization, controlled by ionization constants  $K_{a2}$ ,  $K_{a3}$ ,  $K_{b2}$ , and  $K_{b3}$ . The ability to simulate ionization, the dissociation of a chemical into charged species, may be critical for chemicals that exhibit different chemical characteristics in different ionic states. For some chemicals, such as ammonia or hydrogen cyanide, it may be necessary to predict ionization in order to predict variations in toxic effects.

### Volatilization

105. Volatilization is the flux of a chemical across the air-water interface. The rate of volatilization is proportional to the gradient between the dissolved concentration in the overlying atmosphere. For most chemicals, the partial pressure in the atmosphere may be considered negligible. Volatilization is often treated like surface oxygen exchange, where the loss due to volatilization ( $S_v$ ) is equal to the difference in chemical concentrations multiplied by a transfer coefficient,

$$S_v = k_v(C_w - C_a) \quad (33)$$

where

$k_v$  = transfer rate

$C_w$  = dissolved concentration of the chemical in water

$C_a$  = saturation concentration

Term  $C_a$  is dependent upon the atmospheric concentration and Henry's Law constant for the material.

106. The transfer rate is usually computed as the reciprocal of the resistances in the two films (gas and liquid), as

$$k_v = (R_L + R_G)^{-1} \quad (34)$$

where

$R_L$  = liquid phase resistance

$R_G$  = gas phase resistance

The liquid and gas transfer coefficients are dependent on turbulence at the interface, on temperature, and on properties of the chemical such as diffusivity. Empirical correlations have been developed relating transfer coefficients either directly to physical parameters (such as wind velocity and the density and viscosity of the water (Mackay and Yeun 1983, Southworth et al. 1979), plus the molecular weight and diffusivity of the chemical), or to the field-measured transfer coefficients of oxygen and water vapor (Liss and Slater 1974). O'Connor (1983) presented a theoretical development for the liquid transfer coefficient applicable to a wide range of hydrodynamic conditions.

107. Studies of the loss of volatile organic compounds from CDFs have recently been conducted by Thibodeaux (1989). Generally, volatilization rates from the surfaces of moist surficial solids greatly exceed those in water columns of any appreciable depth.

#### Hydrolysis

108. Hydrolysis is a reaction in which cleavage of a molecular bond occurs in the chemical and a new bond forms with either the hydrogen or the hydroxyl component of a water molecule. Hydrolytic reactions are usually catalyzed by acid and/or base. The overriding factor affecting hydrolysis

rates at a given temperature is generally hydrogen or hydroxide concentration (Wolfe 1980). The overall hydrolysis rate constant is generally calculated by

$$K_H = \sum(k_{HAi} \cdot [H^+] + k_{HNI} + k_{HBI} \cdot [OH^-]) \quad (35)$$

where

$k_{HAi}$  = acid hydrolysis rate constant for phase i,  $\ell \text{ mole}^{-1} \text{ sec}^{-1}$

$[H^+]$  = hydrogen ion concentration, moles  $\ell^{-1}$

$k_{HNI}$  = neutral hydrolysis rate constant for phase i,  $\text{sec}^{-1}$

$k_{HBI}$  = alkaline hydrolysis rate constant for phase i,  $\text{mole}^{-1} \text{ sec}^{-1}$

$[OH^-]$  = hydroxide ion concentration, moles/ $\ell$

### Photolysis

109. Photodegradation (photolysis) is the transformation or degradation of a compound that results directly from the adsorption of light energy. Its rate is a function of the quantity and wavelength distribution of incident light, the light adsorption characteristics of the compound, and the efficiency at which absorbed light produces a chemical reaction. Photolysis is classified into two types that are defined by the mechanism of energy absorption. Direct photolysis is the result of direct absorption of photons by the toxic chemical molecule. Indirect or sensitized photolysis is the result of energy transfer to the toxic chemical from some other molecule that has absorbed the radiation.

110. A quantitative framework that permits the prediction of direct photolysis from the incident light and the characteristics of the chemical (Zepp and Cline 1978) has been incorporated into several toxic chemical modeling frameworks. Use of this framework in natural water systems is complicated by the lack of a satisfactory model of ultraviolet light penetration that incorporates the effects of both dissolved organics and particulate material in the water column. A comprehensive framework for photolysis also must include sensitized photolysis. Unfortunately, the spectrum of compounds, particularly dissolved organics, involved in photochemical reactions is not known (Miller 1983). In addition, valid frameworks to predict free radical reactions have not been developed, and the importance of these reactions remains undetermined (Zepp 1980).

111. A less rigorous method for predicting the photolysis rate coefficient  $K_p$  involves extrapolations of observed rates from one environmental condition to another, as described by

$$K_p = K_{PG}[L]\sum(\Phi P_i) f_i \quad (36)$$

where

$K_{PG}$  = observed rate coefficient for a reference light intensity,  $\text{sec}^{-1}$

$[L]$  = fraction of reference light intensity averaged through the water column

$\Phi P_i$  = relative yield for the chemical in phase  $i$

$f_i$  = fraction of total chemical concentration in phase  $i$

The reference light fraction  $[L]$  accounts for depth, light extinction, cloud cover, latitude changes, and surface light variability.

#### Biodegradation

112. Biodegradation encompasses the broad and complex processes of enzymatic attack by organisms on organic chemicals. Bacteria, and to a lesser extent fungi, are the mediators of biological degradation in surface water systems. Dehalogenation, dealkylation, hydrolysis, oxidation, reduction, ring cleavage, and condensation reactions are all known to occur either metabolically or via organisms that are not capable of utilizing the chemical as a substrate for growth. Biodegradation is generally assumed to follow Michaelis-Menten enzyme kinetics. Values for the half saturation constant  $K_m$  and the maximum rate of degradation are not easily measured. Toxic chemical models generally assume that the chemical concentration is much less than the half saturation constant and simplify the Michaelis-Menten equation to

$$K_B = -K_B W \quad (37)$$

where  $K_B$  is the second-order rate coefficient ( $\text{ml cells}^{-1} \text{day}^{-1}$ ). The bacterial activity,  $W$  ( $\text{cells ml}^{-1}$ ), is fundamentally the concentration of the enzyme reacting with the toxic chemical. Enzyme concentration cannot be measured in the field, however, and the environmental and ecological effects on its activity are difficult to estimate (Lewis et al. 1984).

113. The growth kinetics of the bacterial population degrading a toxic chemical are not well understood. The presence of competing substrates and of

other bacteria, the toxicity of the chemical to the degrading bacteria, and the possibilities of adaptation to the chemical or cometabolism make quantification of changes in the population difficult. As a result, toxic chemical models generally assume a constant biological activity rather than modeling the bacteria directly. Often, measured first-order biodegradation rate constants from other aquatic systems are used directly.

#### Oxidation-reduction

114. Chemical oxidation of organic materials can be a consequence of interactions between free radicals and the pollutants. Free radicals can be formed as a result of photochemical reactions. Free radicals that have received some attention in the literature include alkylperoxy radicals ( $RO_2$ ), OH radicals, and singlet oxygen. Oxidation is often modeled as a second-order process dependent upon concentration of the oxidant and chemical.

### Contaminant Transformations - Inorganic Chemicals

#### Overview

115. Trace metals are often associated with contaminated solids. Lyman et al. (1987), in surveys of sediment quality in the United States, found that heavy metals were the most frequently mentioned contaminant, with over 69 percent of sites having one or more heavy metals present. Bird (in preparation), in surveys of US Army Engineer District offices, found that metals were mentioned as a problem at 79 percent of dredging sites.

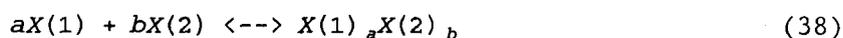
#### Fate processes

116. Metals may occur as different species, having different mobilities and toxicological effects. Metal speciation may change due to complexation, precipitation, sorption, and redox reactions. Physical loss can be caused by settling and sedimentation, whereas a physical gain may be caused by resuspension.

117. Metal complexation, precipitation. Heavy metals can form complexes with organic and inorganic ligands and precipitate or dissolve. At equilibrium, the distribution of metals among the possible complexes is controlled by the amount of metal and ligands present and the reaction coefficients and solubility products. In natural waters, sorption also affects the distribution by reducing the amount of metal available for complexation and precipitation.

118. Complexation reactions can affect transport by either increasing or decreasing the soluble fraction. Sometimes one chemical species is known to be much more toxic than another for a given heavy metal. This is especially important because some states and the US Environmental Protection Agency have been moving toward "site-specific water quality standards," in which chemical speciation will be considered on a site-by-site basis. For example, a site that is known to have a great deal of naturally occurring dissolved organics may not require as stringent a water quality standard because the dissolved organic material may complex the heavy metal and render it nontoxic to biota.

119. Complexation, the reaction of a metal (e.g., Ag, Cd, Cu, Pb, Zn) with organic and inorganic ligands (e.g., OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NH<sub>3</sub>, S<sup>2-</sup>, amino acids, humates, fulvates) in water to form a third species (the metal-ligand complex), can be described by



and

$$C(i) = k(i) X(1)^a X(2)^b \quad (39)$$

where

a,b = stoichiometric coefficients for the complex

X = metal or ligand activity (or concentration if ionic strength is zero)

C(i) = i<sup>th</sup> complex

k(i) = stability constant for the i<sup>th</sup> complex

120. The reaction may be written in more general form as

$$C(i) = k(i) \prod_{j=1}^N X(j)^{a(i,j)} \quad (40)$$

where

N = total number of components (metals and ligands)

a(i,j) = stoichiometric coefficient for j<sup>th</sup> component of i<sup>th</sup> complex

The total concentration of a particular component distributed among M species (i = 1 to N) is then written as

$$X_T(j) = \sum_{i=1}^M a(i,j) C(i) \quad (41)$$

121. Models such as MINTEQA1 (Brown and Allison 1987) solve these equations through estimating the activity (or concentration) of each of the  $j$  components, computing the concentration of the individual species, using Equation 40, and the total of each component calculated (Equation 41), which is then compared to the known total for all components.

122. Sorption. Heavy metals frequently adsorb or "bind" to solid surfaces. The mechanism of sorption or attachment is via (a) physical absorption to solid surfaces, (b) chemical sorption or binding by ligands at the solid-water interface, or (c) ion exchange with an ion at the solid water interface. In addition, if the heavy metal is complexed in solution by an organic ligand, it could sorb into the organic solid phase much like an organic pollutant. The mathematical formulation for describing the partitioning of a heavy metal between the solid phase and the aqueous phase is the same as for organic chemicals except the  $K_{pi}$  is usually called the "distribution coefficient" for heavy metal (although it may be referred to as the partition coefficient or the binding constant in some cases). In most measurements and simulation models, all soluble complexes are lumped with the free ion to give the dissolved metal concentration. Precipitated metal is lumped with all sorbed species to give the total particulate metal concentration. A spatially variable, lumped distribution coefficient ( $K_D$ ) describes the distribution between the two phases. However, there is inconsistency in reported  $K_D$  values in the natural environment; thus, site-specific values should be used when possible.

123. For inorganic chemicals the partition coefficient is a function of the activity of the chemical, such as the free metal ion, which varies with the chemical composition of the solution. Surface properties, such as cation exchange capacity, and other factors affect inorganic sorption. Therefore, the computation of partitioning normally requires the use of an equilibrium sorption model such as MINTEQA1 (Brown and Allison 1987).

124. A standard relationship for metals sorption may be written as



and

$$K_{AM} = \frac{\{MS_m\}}{[M]\{S_m\}} \quad (43)$$

where

$S_m$  = an adsorbing surface of type m

$K_{AM}$  = standard adsorption constant

[M] = free metal ion concentration

Other models proposed to describe adsorption include the activity Langmuir sorption, activity Freundlich, ion exchange sorption, constant capacitance, and triple-layer surface complexation models (Brown and Allison 1987).

125. Redox reaction. Metals can change oxidation states through various oxidation and reduction reactions. Under some conditions, the kinetics of oxidation or reduction may be important to simulate. Oxidation and reduction may be expressed as



where

$M^{++}$  = oxidized metal

$e^-$  = electron

$M^+$  = reduced metal

$K_{ri}$  = equilibrium coefficient for reaction i

Oxidation-reduction reactions exert significant controls on the chemistry and mobility of major ions and trace metals and their mobility, particularly between suspended and bed solids forms (Medine and McCutcheon 1989). Reduction reactions, such as in the formation of sulfides in benthic layers, may strongly affect the dissolved concentrations and ecotoxicity of trace metals. Redox reactions are generally included in chemical equilibrium models, such as MINTEQA1 (Brown and Allison 1987).

### PART III: MODELS

126. The first steps in the modeling process are model identification and selection. The goals are to identify the simplest conceptual model that includes all the important phenomena affecting exposures and releases from CDFs. Selection of too simple a model can result in inaccurate predictions of releases and exposure concentrations. This can happen even if the model calibration "fits" existing data. Inaccurate projection from present to future can be caused by a changing balance among important processes, such as carbonaceous, nitrogenous, and sediment oxygen demand. The result is a CDF that is either too expensive or underprotective of water quality.

127. On the other hand, selection of too complex a model will most likely result in misdirected study resources, delays in the study, and increased cost. Predictive uncertainty may increase because of extra "free" model parameters that cannot be estimated with available data. Study costs will increase because of the additional data requirements and the expanded computer time and manpower needed for model runs, analysis, and sensitivity studies.

128. No single method presently available considers the myriad of processes that impact releases and exposure concentrations from CDFs. Processes will vary between upland and in-water CDFs, as well as during filling and over the course of the ecological successional history following filling. However, methods and models are presently available to address certain issues concerning CDFs, or can be adapted for that application. Discussed below are modeling strategies used in previous applications, as well as generally available models that may be applicable to CDFs.

#### Previous Studies

129. Simplified methods are available, some of which were described in this report, that can be used to provide cost-effective estimates of exposure concentrations and releases of contaminants from CDFs.

130. Predictive methods have been developed by Montgomery (1978, 1979), Montgomery, Thackston, and Parker (1983), and Palermo and Thackston (1988a,b) to estimate solids concentrations in the CDF effluent based on results of column settling tests. Palermo (1986) and Palermo and Thackston (1989a,b) developed predictive methods to estimate contaminant concentrations from

dredged materials using a modified elutriate test. Ludwig and Sherrard (1988) evaluated the standard elutriate test as an estimator of contaminant release at the point of dredging. The column settling and modified elutriate tests should provide a practical means of estimating solid and contaminant concentrations in releases of existing CDFs, where the conditions in the CDF are properly characterized, as well as information useful for CDF design. The laboratory methods have been verified with field data.

131. The laboratory techniques provide estimates of solids and contaminant concentrations in waters directly discharged during dredging operations. Predictive methods are also often required for discharge quantity and quality through indirect mechanisms, such as through the dike wall, during operating as well as nonoperating conditions, and through transformation/degradation processes. The relative importance of these processes is often difficult to assess from laboratory or field experiments alone. Mathematical models often provide the most viable predictive framework for estimating the consequences and relative importance of the processes impacting contaminant losses and release. The results of laboratory studies can be incorporated into mathematical models to provide an integrated predictive framework.

132. Simplified mathematical models of CDFs have been developed by Mills et al. (1985), Environmental Laboratory (1987), USAED, Chicago (1987), Martin, Ambrose, and McCutcheon (1988), McCutcheon, Ambrose, and Martin (1988), and Roth and Fink (1988). These models have been applied in screening mode to estimate the releases of contaminants such as PCBs and, in the case of studies by Roth and Fink, the associated human health risk.

133. The modeling technique by the Environmental Laboratory (1987) was designed to provide a screening method for comparison and order of magnitude appraisal of CDFs. Formulations were developed for both operating and nonoperating conditions. The technique treated PCBs as a conservative material (did not consider transformation-degradation processes such as volatilization or biodegradation) and did not consider the adsorption/desorption of PCBs from solids. Inflows were estimated from sediment characteristics and dredging operations, and outflows were estimated from sediment loadings and water displacement. Changes in pond volumes in response to solids loadings were calculated. During the nonoperating phase, the losses of PCBs through the dike to the surrounding water body were estimated. The approach was applied to estimate loadings from Saginaw Bay, Lake Huron.

134. McCutcheon, Ambrose, and Martin (1988) developed a steady-state spreadsheet model to estimate the effects of initial dilution due to dredging and disposal on contaminant concentrations of hydrophobic organics, such as PCBs. Their model was based on partitioning theory and included estimates of exposure concentrations in the CDF and at the dike face. Also included were methods for estimating the retardation of flows due to sorption within the dike. Their model was applied to the proposed Indiana Harbor CDF.

135. The USAED, Chicago (1988), developed spreadsheet models to simulate releases from the Chicago CDF and to estimate potential releases from a proposed CDF in Waukegan Harbor. The Chicago District's model was particularly detailed in methods used to estimate the formation of deltas in the CDF during the operational phase. Delta formation will impact the hydraulic driving force for dike seepage, benthic-water column interactions, and other processes impacting contaminant exposure and release. Their modeling study also contained algorithms estimating the release of contaminants from benthic interstitial waters due to squeezing of pore waters from consolidated benthic materials and from drainage of dredged materials placed on deltas above the waterline. Seepage estimates were made using Darcy's equation, while pumpage was estimated from design capacity or available capacity of a local treatment plant. Several alternative designs were evaluated for the proposed Waukegan Harbor CDF.

136. Martin, Ambrose, and McCutcheon (1988) incorporated algorithms into the Water Analysis Simulation Program, Version 4 (WASP4) (Ambrose et al. 1988b) to simulate exposure concentrations and releases from CDFs. The formulations were based in part on the modeling studies by the Environmental Laboratory (1987), which were incorporated into the generalized format of the WASP4 model. The revised model structure allowed simulation of the water balance in order to estimate discharges over a weir and through a porous dike as well as for pumping, solids transport and sediment/water quality interactions, and the effects of sorption, volatilization, biodegradation, and other processes on exposure concentrations and contaminant releases. Demonstration simulations were conducted for proposed CDFs in Waukegan and Indiana Harbors and for an existing CDF in Saginaw Bay, Lake Huron.

137. Roth and Fink (1988) conducted risk assessment calculations to estimate human health risks associated with PCB releases from CDFs. They also conducted screening-level calculations of PCB releases from CDFs into Lake Michigan.

138. The modeling approaches described above are all essentially unvalidated in that they have not been rigorously applied to sites for which sufficient supporting data were available to test that application, particularly with regard to indirect discharges. A possible exception is the approach employed by the Chicago District, which was applied to a limited data base for ammonia releases from the Chicago CDF (Miller 1986).

139. Although designed for structural rather than environmental considerations, models of the consolidation of dredged materials should be applicable to estimate some of the processes impacting contaminant exposure and releases. Johnson (1976) and Cargill (1985) developed mathematical models of the consolidation/desiccation process in confined disposal facilities. Cargill provided documentation of the PCDDF model and computer code as well as discussion of applications to several sites, both in-water and upland. Cargill predicted material heights, both consolidated and unconsolidated, as well as material desiccated. These approaches should be useful in estimating the mounding in CDFs and its subsequent effect on discharges as well as seepage from consolidated dredged materials and evaporative losses.

#### Applicable Models

140. In addition to the methods described above, additional models are available to address processes impacting contaminant releases from CDFs. No single model is available that will simulate all of the transport characteristics of CDFs. However, the factors affecting that transport are reasonably well known and can be incorporated into available models. The number of candidate models is large since the potential release pathways and factors affecting exposure concentrations are numerous. Therefore, a complete review of all applicable models is beyond the scope of this report. Instead, several candidate models will be discussed and guidance provided, wherever possible, on sources of additional information to aid in model selection. For convenience, these models are roughly characterized as models of porous media, contaminant transport and transformations, and biological interactions. Considerable overlap occurs, however, particularly for some generalized modeling approaches.

#### Porous media

141. One area of modeling that has undergone extensive development in recent years is the prediction of flows and transport in porous media. Models

are available to provide estimates of flows through caps placed on CDFs and through landfill structures, as well as for use in "traditional" groundwater analysis.

142. For those CDFs that are filled and to which a cap and cover are applied following closure, the amount of seepage expected from a CDF is directly related to the effectiveness of the cap and cover. Water that penetrates the cap will produce a hydrostatic gradient. Therefore, assessment of postclosure seepage requires the availability of techniques to estimate drainage from and percolation through the design cap and cover.

143. The Hydrologic Evaluation of Landfill Performance (HELP) (Schroeder et al. 1984) model provides seepage estimates. The HELP model is a quasi-two-dimensional hydrological model of water movement across, into, and out of landfills. The model accepts climatologic, soil, and design data and uses a solution technique that accounts for the effects of surface storage, runoff, winter cover, infiltration, percolation, evapotranspiration, soil moisture storage, and lateral drainage. This model is particularly applicable to upland CDFs or in-water CDFs following closure. Both Environmental Laboratory (1987) and the USAED, Chicago (1987), used the HELP model to estimate seepage during nonoperational periods for in-water CDFs. Similarly, the Pesticide Root Zone Model (PRZM) (Carsel, Smith, and Mulkey 1984) consists of hydrology and chemical transport components that simulate runoff, erosion, plant uptake, leaching, decay, foliar washoff, and volatilization of pesticides. PRZM can also be used to estimate percolation and runoff for exposed surfaces in CDFs. Recently, PRZM has been coupled with models of the vadose zone and saturated groundwater, culminating in the development of the RUSTIC model. This model may be useful for simulating postclosure releases for both upland and in-water CDFs.

144. Losses through groundwater transport can be significant in many situations. A number of groundwater models are available for simulating the movement of seepage losses through the subsurface. Van Genuchten (1978) and van Genuchten and Alves (1982) reviewed available models and their application to landfill siting. Gronow, Schofield, and Jain (1988) compiled papers reviewing engineering and environmental issues concerning land disposal of hazardous wastes; Deb and Snyder (1988) reviewed modeling approaches applicable to hazardous waste sites. Van der Heijde, El-Kadi, and Williams (1988) discussed the status of groundwater models and provided an overview and summary listing of available models, including those for saturated flow, variably

saturated flow, and solute and heat transport, as well as hydrochemical, fractured rock, and multiphase flow models.

145. Two models that have recently become available are FOWL and FASTCHEM, developed by EPRI and Battelle Pacific Northwest Laboratories. The models are designed to estimate the leaching of materials from ponds or landfills, while FASTCHEM also models transport of the materials. FASTCHEM was primarily designed to model leachate migration from utility fossil-fuel combustion waste impoundments through natural soil and aquifer materials. These models are not in the public domain.

#### Models of chemical transport/transformations

146. In addition to assessing flow and transport through porous media, a number of models are available to aid in determining chemical transport and their effects primarily in surface waters. These models may be useful for adapting to CDFs or in assessment of the impact of CDF releases on the containing water body.

147. A model available to aid in assessing discharges and their effects is SARAH (Vandergrift and Ambrose 1988), a steady-state mixing zone model that calculates acceptable concentrations of hazardous wastes discharged to land disposal or wastewater treatment facilities. For steady or branch streams, SARAH considers the following concentration reductions: dilution and loss during groundwater discharge; initial Gaussian mixing at the edge of a stream; lateral and longitudinal dispersion; sorption; volatilization; hydrolysis; and bioaccumulation in fish. The model would be applicable to estimating treatment requirements for upland CDFs.

148. WASP4 is a general multidimensional model that uses compartment modeling techniques (Ambrose et al. 1988b). Operated in either the quasi-dynamic or steady-state mode, the user must supply initial volumes, network flow fields, and inflow time functions. The user also must calibrate dispersion coefficients between compartments. Depending on the process model with which it is linked, WASP4 has the capability of simulating a range of conventional and toxic pollutants. Problems that have been studied using WASP4 include BOD, DO dynamics, nutrients and eutrophication, bacterial contamination, and toxic chemical movement.

149. TOXI4 is a version of WASP4 that was designed to simulate organic chemicals and heavy metals (Ambrose et al. 1988a). TOXI4 was created by adapting the kinetic structure of EXAMS-II (Burns, Cline, and Lassiter 1982;

Burns and Cline 1985) to the transport framework of WASP4 and adding solids balance algorithms. It can simulate up to three chemicals and three solids classes. In addition to segment volumes, flows, and dispersive exchanges, the user must supply suspended solids deposition and scour rates, bed velocity, water/benthic layer exchange coefficients, and bottom materials/pore water exchange coefficients. TOXI4 was modified by Martin, Ambrose, and McCutcheon (1988) to model exposure concentrations and releases from CDFs in the Great Lakes.

150. EUTRO4 is a version of WASP4 that was designed to simulate conventional pollutants. EUTRO4 combines a kinetic structure adapted from the Potomac Eutrophication Model with the WASP transport structure. EUTRO4 predicts DO, carbonaceous BOD, phytoplankton carbon and chlorophyll a, ammonia, nitrate, organic nitrogen, organic phosphorus, and orthophosphate in the water column and, if specified, the underlying bed. The modeling approach developed for CDFs by Martin, Ambrose, and McCutcheon (1988) could be coupled with EUTRO4 where predictions of conventional pollutants are required.

151. Assessment of metals impacts is often necessary. Bird (in preparation) stated that 79 percent of Corps offices surveyed indicated that they had metals problems associated with dredging operation. Also, 79 percent had problems with PCBs, 37 percent with PAHs, and 21 percent with pesticide contamination.

152. A number of metals equilibrium models are available for screening sites and estimating speciation. MINTEQA1 (Brown and Allison 1987) is a geochemical model that calculates equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states, and precipitation/dissolution of metals. This model would be useful in estimating metals speciation and its effects on the sorption and mobility of metals as well as their toxic effects.

153. Modeling approaches similar to TOXI4 are presently not available for simulating the dynamic transport and transformations of metals. Instead, models such as MINTEQA1 are used to estimate a "distribution coefficient" for the heavy metals. In most measurements and simulation models, all soluble complexes are lumped with the free ion to give the dissolved metal concentration. Precipitated metal is lumped with all sorbed species to give the total particulate metal concentration. A spatially variable, lumped distribution coefficient  $K_p$  describes the distribution between the two phases. There is

no general consistency in reported  $K_D$  values for particular methods in the natural environment.

#### Biological interactions

154. A major concern of chemical contamination is its human health and ecological effects. Generally, human health is of initial concern, and toxicity and risk characterization is part of any contaminant assessment exercise. For example, Roth and Fink's (1988) assessment of selected Great Lakes CDFs, as part of the studies conducted by the USEPA Great Lakes National Program Office, included risk characterization for PCBs.

155. Many organic contaminants bioconcentrate and bioaccumulate, resulting in increased concentrations that may pose human health and ecological risks. Biouptake and bioaccumulation of contaminants in aquatic organisms can be estimated using available modeling techniques such as those incorporated in the models FGETS (Barber and Suarez 1989) and WASTOX, PART II (Connolly and Thomann 1984).

156. FGETS and WASTOX, Part II - the Food Chain Model, are models that simulate the bioaccumulation of nonpolar organic chemicals by fish from both the water and food. The WASTOX model, in addition, simulates the transfer of those contaminants through the food chain. These models would be useful in assessing the bioaccumulation of contaminants by organisms both within and near CDFs.

157. A generalized model of terrestrial effects has recently been developed, referred to as the Terrestrial Ecosystem Exposure Assessment Model (TEEAM, Dean et al. 1988). The TEEAM simulates toxic organic chemical exposures to wildlife with particular emphasis on passerine birds in agricultural settings. Other available ecological models were reviewed, and criteria to aid in their selection were provided by Mittelman et al. (1987).

#### PART IV: SUMMARY AND RECOMMENDATIONS

158. The processes impacting exposure concentrations and releases due to disposal of contaminated dredged materials in confined disposal facilities are complex. This is due in part to the variety of chemicals and operational and design considerations involved. However, methods are required to estimate those exposures and releases for permitting purposes as well as to aid in the evaluation of alternative designs or operations.

159. Many of the important processes impacting releases of contaminants from CDFs and their effects are reasonably well known. Laboratory column settling and elutriate techniques have been developed to estimate solids and contaminant concentrations in waters directly released during dredging operations (Montgomery 1978, 1979; Montgomery, Thackston, and Parker 1983; Palermo 1986; Palermo and Thackston 1988a,b; Palermo and Thackston 1989a,b). Techniques have been developed to estimate the consolidation/desiccation of dredged materials (Johnson 1976, Cargill 1985). Processes impacting the transport and transformation of inorganic and organic contaminants have received considerable attention and been incorporated into a number of modeling techniques, primarily for surface waters. However, relatively few attempts have been made to consolidate these process descriptions into a unified mechanistic modeling approach applicable to CDFs. Modeling studies have been attempted by the US Army Corps of Engineers (Miller 1986; Environmental Laboratory 1987; US Army Engineer District, Chicago 1987) and the US Environmental Protection Agency (Martin, Ambrose and McCutcheon 1988; McCutcheon, Ambrose, and Martin 1988; Roth and Fink 1988). These studies have proved valuable in estimating the impacts of Great Lakes CDFs, as well as providing a common ground for discussion. However, these approaches are largely unvalidated. No database of sufficient detail to evaluate their applications presently exists.

160. Some combination of the models and methods presently available may be sufficient to provide reconnaissance-level evaluations of the impacts of CDFs. However, additional model development, such as in the area of hydraulic pumping as well as supporting field and laboratory development, is required to develop fully predictive tools. Such tools would provide cost-effective methods for evaluating the effects of CDFs, as well as design and operational alternatives.

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